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ABSTRACT

Copper-based fungicides (Cu_f) are used in European (EU) vineyards to prevent fungal diseases. Soil physicochemical properties govern locally the variation of total copper content (Cu_t) in EU vineyards. However, variables controlling Cu_t distribution at larger scale are poorly known. Here machine learning techniques were used to identify governing variables and to predict the Cu_t distribution in EU vineyards. Precipitation, aridity and soil organic carbon are key variables explaining together 45% of Cu_t distribution across EU vineyards. This underlines the effect of both climate and soil properties on Cu_t distribution. The average net export of Cu at the EU scale is 0.29 kg Cu ha^{-1} which is two orders of magnitude less than the net accumulation of Cu (24.8 kg Cu ha^{-1}). Four scenarios of Cu_f application were compared. The current EU regulation with a maximum of 4 kg Cu ha^{-1} $year^{-1}$ may increase by 2% the EU vineyard area exceeding the predicted no-effect concentration (PNEC) in soil in the next 100 years. Overall, our results highlight vineyard areas requiring specific remediation measures and strategies of Cu_f use to manage a trade-off between pest control and soil and water contamination.

INTRODUCTION

Copper-based fungicides (Cu_f) are intensively used in European vineyards since the end of the 19th century to prevent fungal disease such as 'Downy Mildew'.[1] Cu_f application doses and timing vary across regions depending on practices, regulation, hydro-climatic conditions and vine variety. The European Union (EU 2018/1981) regulation recently decreased from 6 to 4 kg Cu ha^{-1} year^{-1} the maximal dose allowed.[2] However, doses as high as 50 kg Cu ha^{-1} year^{-1} were applied frequently for decades in the mid-20th century.[3] Today, the total copper content in topsoil (Cu_t) exceeds 100 mg Cu kg^{-1} in 15% of the European vineyard area. This corresponds to the average proposed threshold values for which soil remediation is needed.[4-6] European vineyards represent more than 50% of the total vineyard surface worldwide.[7] Although vine growing accounts for only 3.3% of the agricultural area in Europe, it uses 86% of total fungicides consumed in Europe.[8] Hence, vineyard soil is often more contaminated by Cu_f than soils of any other agricultural soils. Cu_f accumulates in soil and can impact soil organisms and plants,[9] thereby reducing soil fertility[10] and productivity.[11] In contrast, leaching[12] and surface runoff[13,14] export Cu_f from vineyard soil, which can contaminate aquatic ecosystems[15] and drinking water resources.[16]

Cu_f mobility in topsoil controls Cu_t accumulation and off-site export. Cu mobility in soil is mainly controlled by (i) sorption on organic matter,[17] and to a lesser extent on clay and Fe-, Mn-(hydr)oxide and carbonate,[18] (ii) pH-redox dependency since alkaline soil increase the proportion of available binding sites on organic matter.[17,19] Cu sorbed on fine particle matter may result in Cu export in runoff. [13,14] Hydro-climatic and field conditions indirectly control Cu export by (i) affecting soil properties,[20] (ii) mediating

dissolved and particulate Cu_f transport, and (iii) modifying preferential transport.[21] Accordingly, presumed or established processes governing Cu_t mobility in vineyard soil may co-occur and/or may be interrelated (Table 1). Variables governing Cu_t and dynamics in vineyard soil are, however, examined in laboratory and field studies separately. As a result, the understanding of variables governing Cu_t in soil remains study- or site-specific. The identification of variables governing Cu_t in vineyard soil and leading to Cu accumulation and/or off-site export over time is necessary to evaluate the current and future distribution of Cu_t at the European scale.

In this context, a major issue is to predict the spatial variation of Cu_t in the European vineyards, to quantify Cu accumulation and export and to identify priority areas requiring soil remediation. The purpose of this study was (i) to identify key variables potentially governing Cu_t in vineyard topsoil (0 – 30 cm), (ii) to predict average Cu_t at European vineyards scale using machine learning technics, and (iii) to estimate Cu_t accumulation, export and associated toxicity for terrestrial trophic levels, for historical, current and future scenarios of Cu_f application (i.e, 0, 2, 4 or 8 kg Cu ha^{-1} y^{-1}).

MATERIALS AND METHODS

Topsoil total Copper Datasets.

Cu_t datasets ($Cu_{t,\ dat}$; i.e., soils within 0–30 cm) were obtained from several soil surveys across European vineyards (–9.4° to 42° E; 35° to 53° N; SI, Figure S1) delineated by the Corine Land Cover (CLC 2012; v18.5.1; http://land.copernicus.eu). In total, 1,202 $Cu_{t,\ dat}$ measurements (average: 27.8 mg Cu kg^{-1}; min–max: 0.54–774 mg Cu kg^{-1}) were sampled between 1992 and 2016 (median = 2008, standard deviation

(SD) = 5) and used in our study. Summary of the studied $Cu_{t,\ dat}$ are provided in Table S1 of the Supporting Information (SI). Although the Cu quantification methods differ among datasets, inter-comparability between datasets has been demonstrated previously for the methods used in our study.[22] The impact of topsoil sampling depth (first 20 or 30 cm) and sampling time span on the average prediction of Cu_t (Cu_{pred}) at the European scale remains low (SI, section Influence of heterogeneous sampling depths and time on the Cu prediction). The heterogeneity of topsoil sampling depth and time span did not significantly (within 2σ) impact the average predictions of Cu_t at the European scale.

Predictive Variables.

Soil properties, topology, climate and land cover were selected and evaluated as hypothetic predictive variables of Cu_t (Table 1 & SI, Table S2). Geogenic, i.e., from bed rocks,[23] and atmospheric non-agricultural anthropogenic inputs of Cu, i.e., mining, smelter, sewage sludge and vehicle brake pads are sources of Cu contributing from 5 to 100 g Cu ha^{-1} $year^{-1}$ whereas about 8 kg Cu ha^{-1} $years^{-1}$ of Cu_f are applied on vineyards.[24] Topsoils surrounding Cu mining or smelter, that may reach up to 6 g Cu kg^{-1},[25,26] were not identified close to vineyard areas. Consequently, geogenic and industrial sources of Cu were not considered in this study.

Table 1. Hypothetic Predictive Variables Governing the Total Copper Content in Vineyard Topsoil (Cu_t) Leading to Cu_t Accumulation and/or off-site Export.

Variables [a]	Processes
Soil properties	
Soil physicochemical properties affect Cu_t mobility	Cu_t correlates positively to soil organic matter since Cu preferentially sorbs to organic matter in soil,[13,17] which affects Cu_t mobility. Higher pH increases sorption sites (e.g. negative charge) for Cu_t on clay, organic matter and sand containing carbonate,[19] and reduces Cu_t leaching.[12]
Soil moisture influences soil biogeochemistry	Soil moisture directly affects microbial respiration and activities in soil resulting in biogeochemical gradients.[27,28] Cu occurs as Cu(II) in oxic soils. In contrast, Cu(II) may potentially precipitate to less mobile Cu(I) forms in anoxic soils.[17,29]
Topography/climate	
Topography and climate conditions drive soil erosion	Greater rainfall depth and higher slope length enhance soil erosion by runoff.[21] Cu_t is mostly bound to suspended particles matter (SPM) in topsoil (~85%[13, 14]) where SPM-bound Cu can account for 84.4% of the total Cu_t exported by runoff.[14]
Hydro-climatic conditions influence Cu application doses	Intense rainfalls during warm conditions favor the development of 'Downy Mildew'. This increases the frequency and amount of Cu_t use in some areas to control it.[30,31]
Hydro-climatic conditions influence (i) soil chemistry	Arid environments (with higher AI values), characterized by higher soil pH and oxidizing soils,[20] favor Cu_t accumulation (see soil physicochemical properties above). In contrast, arid soils tend to lose more soil organic matter and associated Cu_t since Cu is preferentially associated to soil organic matter.[13,17]
(ii) Vegetation growth	Optimal conditions for vegetation growth depend on temperature, soil moisture and solar radiation, and vary across plant growth stages.[32] Vegetation growth controls Cu_t mobility indirectly by limiting erosion via surface runoff and thus can be related to Cu_t.

(iii) Plant uptake	Cu uptake from soil by plants remains limited: 0.1–7.2% by wild[33] and 0.1–3.8% by the vineyard[34] plants of the Cu_t. Hence, plants only marginally decrease Cu_t in soil.
Plant cover	
Plant cover affects surface runoff and organic matter content in topsoil	Plant cover, i.e., vine and grass in vineyards, can stabilize the vineyard soil and thus limit erosion via surface runoff.[35] In addition, plant decomposition can slightly increase organic matter content in topsoil,[36] thereby reducing Cu mobility.

[a] Hypothetic predictive variables governing Cu_t in vineyard soil. Variables associated with each process are provided in the SI, Table S2. Processes were identified based on experimental studies in vineyard or related soil.

Predictive variables were computed or directly obtained on a grid cell of 250×250 m for the study area. Details concerning building spatial variables are provided in the in SI, Table S2 & S3. $Cu_{t,\ dat}$ coordinates were used to extract values of each predictive variable in the corresponding grid cells. Extracted data were then used to select variables and calibrate the model (details in SI). Extracted data represented adequately the range of predictive variables within the prediction domain (details given in SI; paired t-test; $p\text{-value}_{average}$ >0.01) and did not display any spatial correlation (Moran's test; $I_{average} = -0.211 \pm 0.09$; p-value >0.01). The selection of variables was carried out from the 24 original predictive variables (SI, Table S2) to limit collinearity between predictive variables and optimize model predictions as described elsewhere:[37] (i) Pearson correlation was used to discard variables providing the similar information and (ii) principal component analysis (PCA) was used to discard noise variables containing the least information.[38]

Prediction of Total Copper Content in European Vineyard Topsoil.

The variable selection procedure highlight that the following variables were predictive of the average Cu_t in European vineyards: clay and silt fractions (%), soil organic carbon content (C_{org}; %), soil pH (unitless), aridity index (AI; unitless), annual average temperature (T_{av}; °C), annual rainfall (rainfall; mm), soil moisture content (moisture; %), the enhanced vegetation index (EVI; unitless) and slope (degree; SI, Table S3). This selection is consistent with predictive variables reported previously (Table 1). Three independent machine learning techniques, i.e., neural networks (R package nnet v 7.3-12), random forest (R package randomForest v.4.6-12) and bagging tree (R package ipred v.0.9-5), were used in parallel and were averaged into an ensemble model (ENS; details in SI) for the final prediction, as described elsewhere.[39] The ENS resulted in fewer false predictions and higher predictive accuracy than a single model. Consistency of Cu_{pred} was evaluated for each grid cell on a SD of 1,000 predictions for each machine learning technique. Model performance was evaluated using a 10-fold cross-validation (CV). Model spatial transferability was evaluated using a spatially constrained 10-fold CV (details in SI). For each model, the averaged relative importance (ARI) of each variable in the model was calculated with an input permutation technique and one-factor-at-a-time (OFAT) sensitivity analysis (details in SI). The complete modelling framework to select variables, calibrate the model and predict Cu_t is available for download at https://github.com/Boris-Droz/ML_soil_predi_conc.

145

146 **Copper Accumulation and Export.**

147 Cu_t net mass accumulation since the beginning of the Cu_f application was estimated
148 assuming that Cu_t is distributed similarly across a homogenous topsoil layer, following
149 eq. 1,

150 $$net\ acc. = \left(Cu_{Pred} - Cu_{bgd}\right) \times BD \times h_{topsoil} \quad (1)$$

151 where $net\ acc.$ stands for the Cu_t net mass accumulation (kg Cu ha^{-1}), Cu_{bgd} the
152 background of geogenic and atmospheric non-agricultural anthropogenic Cu_t (mg Cu
153 kg^{-1}; SI, Figure S2), BD is the soil bulk density (https://soilgrids.org/, series M_sl1,
154 v18.4.2017; in kg m^{-3})[40] and the average topsoil thickness where Cu mainly
155 accumulates ($h_{topsoil}$ = 30 cm; SI, Table S1). The net mass export of Cu_t ($net\ exp.$; kg of
156 Cu ha^{-1}) was assumed to be the sum of Cu_t exported from topsoil via runoff and
157 leaching, and was calculated yearly following eq. 2,[13, 14]

158 $$net\ exp. = \left(\dot{q}_{RUSLE} + f_{sol} \times BD \times h_{topsoil}\right) \times Cu_{Pred} \quad (2)$$

159 where $\dot{q}_{RUSLE}$ is the soil loss rate (kg ha^{-1}) as defined elsewhere[21] and f_{sol} the soluble
160 fraction of Cu_{Pred} estimated from soil properties (both details in SI).

161

162 **Scenarios of Copper-Based Fungicides Application Doses.**

163 Four scenarios of Cu_f application doses were compared: (i) an historical scenario with
164 8 kg Cu ha^{-1} $year^{-1}$ inferred from sold Cu_f amount before the 2002 European
165 regulation,[2] and/or speculated illegal usage in some areas,[41] (ii) current regulation
166 scenarios, with either (iii) 2 or (iii) 4 kg Cu ha^{-1} $year^{-1}$ as average and maximum doses,

167 respectively,[2, 42] and (iv) a scenario of Cu_f substitution, i.e., no Cu_f application or 0 kg Cu
168 ha^{-1} $year^{-1}$.

169 For the scenario with 8 kg Cu ha^{-1} $year^{-1}$ and current regulation scenarios, a stepwise
170 mass balance calculation based on a year t was established (eq. 3 and detail in SI)
171 assuming no temporal variation of the topsoil volume and a homogeneous topsoil layer
172 (0–30 cm),

173 $$Cu_{pred,t+1} = Cu_{pred,t} + (APP_{Cu,f} - Cu_{pred,t} \times net\ exp. - Cu_{input} \times f_{sol})/(BD \times h_{topsoil}) \quad (3)$$

174 where Cu_{pred} is the average predictions of Cu_t (mg Cu kg^{-1}), $APP_{Cu,f}$ the yearly
175 application dose of Cu_f (kg Cu ha^{-1} $year^{-1}$) and f_{sol} the soluble fraction as calculated in
176 eq S3–6. The $net\ exp.$ was previously calculated in eq. 2. $Cu_{pred,t+1}$ accounted for the
177 yearly Cu application dose to which the soluble fraction of Cu_f (f_{sol}) and the $net\ exp.$
178 were deducted. For each, pixel, the scenario was applied until Cu_{pred} at year $t+1$
179 reaches for the given pixel the predicted no-effect concentration (PNEC; SI, building
180 spatial variables). In contrast, the time required to export the accumulated Cu_f via runoff
181 and associated suspended solids and reach back Cu_{bgd}, i.e., assuming the existence of
182 alternatives to Cu_f, was estimated by dividing eq. 1 by eq. 2.

183 The uncertainty associated with each scenario was estimated by numerical
184 propagation of uncertainties across the entire modelling framework. Briefly, each
185 variable was associated with lower and an upper uncertainty limits accounting for the
186 analytical or monitoring uncertainty or calculation steps, depending on the variable (SI,
187 Table S4). All combinations of lower and upper uncertainty limits for the selected
188 variables were then included to propagate uncertainties and estimate the lower and
189 upper uncertainty limits associated to each scenario for each pixel independently.

RESULTS AND DISCUSSION

Prediction of Total Copper in Topsoil.

Ten variables governing Cu_t in vineyard topsoil were considered (see above Materials and Methods and SI, Figure S4. b). Using these climate and soil variables, the ENS accurately predicted Cu_t (slope of 1.13, intercept of 0.01; SI, Figure S4. a), and predictions were fairly precise (averaged $R^2 = 0.61$). Comparison between ENS and CV (averaged R^2-CV = 0.58 ± 0.06) indicates no over-fitting of the ENS. For the three machine learning technics, Cu_{pred} fit $Cu_{t,\ dat}$ (SD $Cu_{pred}/Cu_{t,\ dat} \times 100 = 13 \pm 2\%$), indicating a good overall agreement of predictions between the three technics. Average uncertainty of the Cu_{pred} falls within ± 11 mg Cu kg^{-1} for 75% of the data (RMSE of 0.63 ± 0.06). The scattering observed in the predictions (SI, Figure S4) mainly concerns data above 130 mg Cu kg^{-1}, corresponding to 6.3% of the dataset only. ENS predictions failed to reproduce observed Cu_t in the corresponding vineyard areas, which potentially received larger historical Cu_f applications than other areas under similar climatic and soil conditions. Additional model performances and limits are provided in SI.

Climate Variables rather than Soil Variables Determine Total Copper in Topsoil.

Climate variables (i.e., rainfall and aridity index) mainly determined Cu_{pred} at the European scale, possibly by controlling physicochemical processes, including Cu leaching and the redox state of soil. Hydro-climatic conditions likely determined regional Cu application practices as ‘Downy Mildew’s’ pressure increases in more humid and

213 warmer areas in early summer.[30,31] In contrast, soil physicochemical properties (i.e., pH)
214 predominantly governed Cu_t on the local scale and under homogeneous climatic
215 conditions. The averaged relative importance (ARI) from the ENS and the sensitivity
216 analyses confirmed the relationship between climate variables and Cu_{pred}. Cu_{pred}
217 correlated positively with both the annual rainfall (rain; R^2 = 0.71) and the aridity index
218 (AI; potential evapotranspiration divided by rainfall; R^2 = 0.79), while the combined
219 effect of rainfall and AI accounted for 32.6% of the Cu_{pred} ARI (rainfall = 17.4 ± 0.9%, AI
220 = 15.2 ± 1.3%; SI, Figure S4. b).

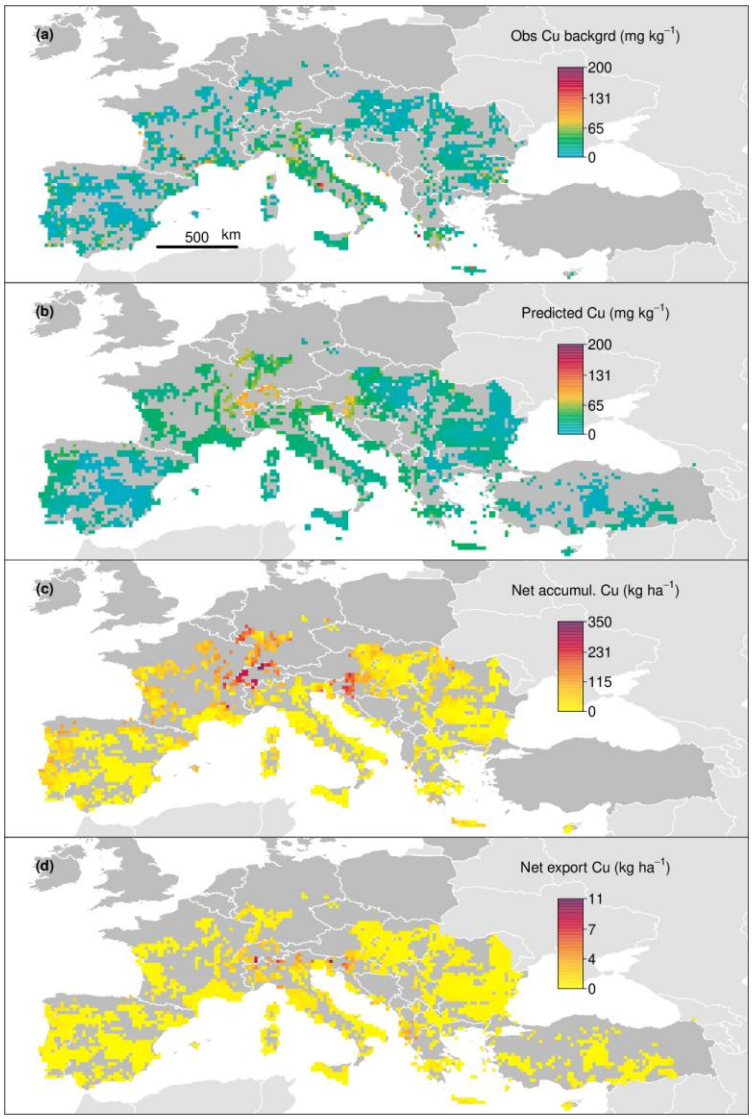
221 Although rainfall was negatively correlated with AI, both variables were positively
222 correlated to Cu_{pred}, suggesting that two different mechanisms control Cu_t in vineyard
223 soil. First, rainfall could increase temporally soil water content and reduce oxygen
224 diffusion in water, leading to reducing soil conditions.[43] Under anoxic conditions,
225 biological activity may decrease Cu mobility by precipitating soluble Cu(II) to Cu(I),[44,45]
226 which is strongly complexed and stabilized with reduced organic sulfur.[46] Additionally,
227 depending on the solutes present in soil, e.g., carbonate, sulphide, biotic and abiotic
228 processes may form minerals and further reduce the Cu_t mobility.[33, 47, 48]

229 In contrast, higher AI leads to drier soil,[49] which facilitates the formation of soil
230 macropores favoring oxygen transfer.[50] As a result, Cu(I) may partly re-oxidize into
231 mobile Cu(II) in oxic soil. However, an opposite trend is observed as AI may indirectly
232 increase the Cu-binding affinity of soil organic matter (ARI of 13.1 ± 0.1%). Indeed, the
233 oxidation of organic matter under oxic conditions increases the contribution of carboxylic
234 and hydroxylic groups as preferential binding partners for Cu in organic matter.[51] In

addition, pH (ARI of 7.5 ± 1.3%) directly controls the deprotonation of sorption sites on soil constituent. Hence, higher pH increases available sorption sites for Cu binding.[19]

Distribution of the Total Copper in Topsoil Across European Vineyards.

Cu_{pred} in European vineyards were successfully made as the datasets covered the range of predictive variables within the domain of prediction. The ENS also displays good model transferability in space evaluated on four equivalent geographical sub-domains (average R^2 = 0.84 ± 0.07, details in SI). This suggests a homogenous influence of predictive variables within the European vineyards. Overall, Cu_{pred} for vineyards is 25.4 mg Cu kg^{-1} which is 30.5% higher than Cu_{bgd} including geogenic and atmospheric non-agricultural anthropogenic Cu (Figure 1. a–b).



247

248 **Figure 1.** Distribution of the total copper content in vineyard topsoil (Cu_t), accumulation
249 and net export of Cu in European Vineyards. (a) Observed background Cu_t. (b)
250 Predicted Cu_t (Cu_{pred}). (c) Estimated net accumulation of Cu_t. (d) Estimated net export of
251 Cu_t. Dark grey: Area of the European Corine Land Cover (CLC). Pixels depict average
252 predictive values at a spatial resolution of 20 km^2. Net accumulation was not computed
253 for Turkey due to absence of background data. Overall, Cu_{pred} were higher for vineyards

254 in the alpine regions (Figure 1. b; average = 57 mg Cu kg^{-1}) than in other European
255 biogeographic regions (SI, Table S5).

256

257 The threshold of contamination (>100 mg Cu kg^{-1})[5] was reached for 2% of Cu_{pred}
258 within the prediction domain. Contaminated areas were mainly located in central
259 Western Europe, i.e., northern Italy, eastern France, Switzerland and Slovenia. In those
260 regions, C_{org} is medium (up to 14%) while Cu_{pred} >100 mg Cu kg^{-1} accounted for 70% of
261 vineyard soil.[52] Data points above the contamination threshold in those regions are
262 characterized by high AI, soil moisture and annual rainfall, although only C_{org} was
263 significantly higher (>9.0%) than in other regions of southern Europe (t-test; p-value
264 <0.01). This suggests that higher annual rainfall correlates with higher temperature in
265 central Western Europe. This may favor 'Downy Mildew' emergence and concomitant
266 use of higher doses and more frequent applications of Cu_f. In central Western Europe,
267 soil with higher C_{org} may influence the Cu_{pred} predominantly and locally, although C_{org}
268 accounted in total for 13.1% ARI of the $Cu_{pred.}$

269

270 **Accumulation and Export of Copper in Topsoil.**

271 The estimated average net accumulation and net export of Cu in topsoil in European
272 vineyards are 24.8 (SD = 42.7) and 0.29 kg Cu ha^{-1} (SD = 0.64), respectively (Figure 1
273 c–d). This corresponds to 112,400 tons of Cu accumulated over time, and a yearly Cu
274 export from vineyards of 1,466 tons across Europe. The distribution of Cu net export
275 fitted with that of Cu_{pred} (R^2 = 0.65). On average, predicted loss rate of vineyard soil
276 (9.47 tons ha^{-1} $year^{-1}$) is 3.5 times greater than any other European arable land due to

low vegetation and sloping area in vineyards. Consequently, net Cu export is particularly large in the Southern Alps due to intense soil erosion. Large soil loss is associated to higher slope (>25°) and greater rainfall amounts (>1,600 mm $year^{-1}$) in the Southern Alps than in other vineyard areas.[21]

Potential Future Copper Accumulation in European Vineyards.

Overall, the proportion of European vineyard area exceeding PNEC values (i.e., ranged from 30 to 290 mg Cu kg^{-1} according to soil properties calculate elsewhere,[53, 54] details in SI) may largely vary in the future depending on the application dose of Cu_f (Figure 2). Cu accumulation due to Cu_f application doses of 2, 4 and 8 kg Cu ha^{-1} $year^{-1}$ may be balanced with Cu export after 1,200, 750 and 150 years, with 75, 89, 97% of European vineyards areas exceeding PNEC values, respectively. Assuming constant soil properties, we speculate that the current European regulation with a maximum application of 4 kg Cu ha^{-1} $year^{-1}$ will increase by only 2% the proportion of vineyard areas exceeding PNEC in the next 100 years.

In contrast, 94% of vineyard areas may exceed PNEC in the historical application scenario of 8 kg Cu ha^{-1} $year^{-1}$. With an application of 2 kg Cu ha^{-1} $year^{-1}$, vineyards areas exceeding PNEC values may increase by less than 0.5% for the next 100 years. In contrast, a substitution of Cu_f (0 kg Cu ha^{-1} $year^{-1}$) may decrease the proportion of vineyard areas exceeding the background Cu_{bgd} from 48 to 38% after 100 years. Such long-term indicative estimation for different Cu application dose provides critical temporal trend to support the reduction of Cu application in vineyard.

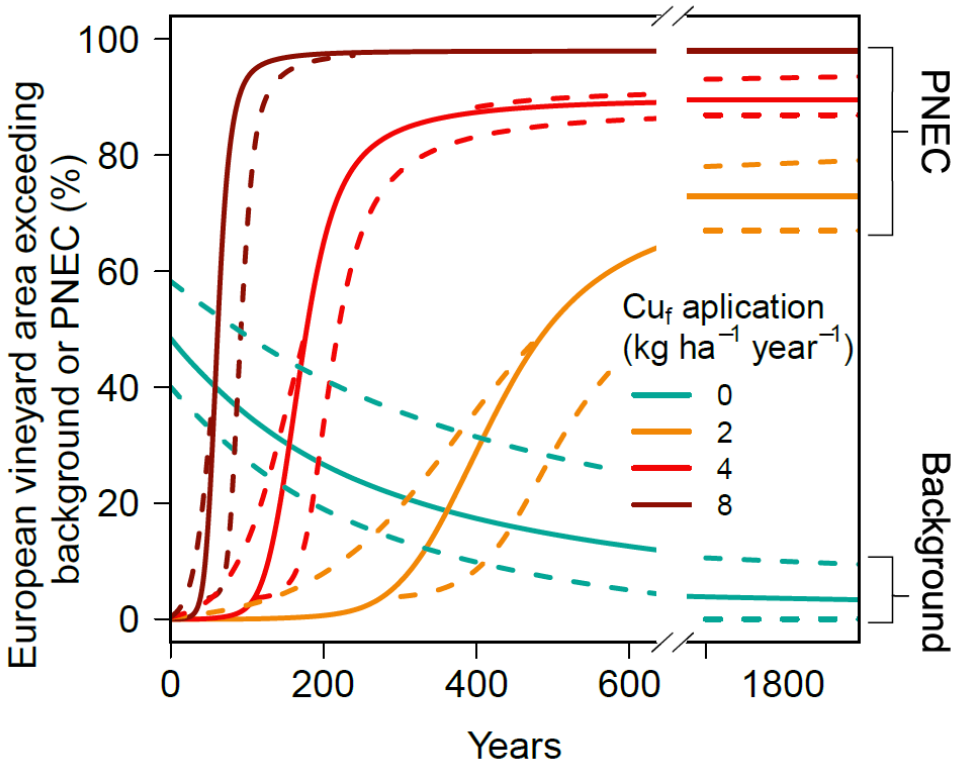


Figure 2. Proportion of European vineyards area exceeding predicted no-effect concentration (PNEC) values of total Cu in topsoil (scenarios with Cu_f application dose of 2, 4, 8 kg ha^{-1} $year^{-1}$) or equal to or lower than the background (bgd) Cu content (scenario with no Cu_f application). Predictions account for the balance between yearly Cu_f application at a given application dose and Cu export over time. Dashed lines indicate the upper and lower uncertainties of predictions.

Our back-envelope is a first attempt to evaluate Cu accumulation and export at the European scale and the proposed mass balance approach may lead to inaccurate estimations of Cu_t export. For instance, freshly applied Cu_f is a soluble Cu pool that can be directly exchanged with the labile cation present in vineyard soil following Cu_f

311 application. Depending on the time following Cu_f application, Cu_f may be partly mobilized
312 during rainfall-runoff events[14] and thus bias estimations of Cu_t in soil. Since rainfall
313 erosivity is predicted to increase by 18% in Europe over time, Cu_f export may also
314 increase.[55] In addition, estimations using the semi empirical model account for Cu aging
315 in contaminated soil and rely on realistic desorption experiments, which may
316 underestimate Cu_f export.[12] However, Cu_f accumulation over time may be also
317 underestimated. Climate change models predict an average of 10% increase of soil
318 organic matter content by 2100 in regions of European vineyards,[56] which may in turn
319 reduce Cu_t mobility and increase the amount of Cu accumulated in the vineyard soil.
320
321 **Implications for Winegrowing Practices.**
322 Cu is an element that cannot be degraded in soil and soil remediation processes,
323 such as phyto-extraction[57] or enhanced mobilization by plants,[58] have limited
324 efficiencies. The most efficient strategies to limit the increase of Cu_t is thus to reduce
325 application doses of Cu_f. Reducing strategies consist in applying Cu_f during long humid
326 periods only[42] and in reducing preventively the use of Cu_f. Forecast models of
327 grapevine 'Downy Mildew'[59] relying on climate variables can help to improve the
328 efficiency of Cu_f reduction strategies. Alternatives to Cu_f include replacing current grape
329 varieties with new grape varieties with a higher resistance to fungus pests,[60] using
330 microorganisms for biocontrol,[61] introducing plant defense stimulators[62] and/or applying
331 plant extracts to substitute Cu_f.[63] Alternative scenarios without Cu_f are still debated, but
332 are currently used in some Biodynamic approaches accounting for only ca. 1% of
333 vineyards worldwide (http://www.demeter.net). Additional benefits of biodynamic wine

growing include the higher soil biodiversity and microbiological activity[10] and potentially greater resilience to climatic and pathogenic threats in vineyards[64] as opposed to most conventional wine growing.[65]

Cu export is mainly driven by soil erosion with concomitant loss of solid-bound Cu, which should be prevented and lessened in regions prone to soil loss to reduce contamination of connected aquatic ecosystems. In fact, 10% of the vineyards are located close to a river (<500 m)[66] and the associated catchment may act as a point source of contamination. The transport of solid-bound Cu into aquatic ecosystems may also affect the downstream areas due to the progressive release of toxic Cu(II) resulting from a change in pH and/or redox conditions. Anti-erosion soil management strategies should thus be prioritized and designed to retain Cu on the vineyard plots. In particular, traditional soil management strategies, including grass or mulch cover, reduced tillage, contour planting and terraced vineyards are most effective in limiting soil erosion and associated Cu runoff.[35] Complementarily, stormwater wetlands may be deployed at the outlet of vineyard catchments. Stormwater wetlands have the potential to retain >68% of the dissolved Cu and >92% of the solid-bound Cu, the principal contributions to Cu export in runoff.[14]

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: XXX/XXXXX.

Texts, tables, and figures provide detailed methods (total copper in the topsoil dataset, spatial variable building, data pre-processing, variable selection, machine learning building, performance and evaluation, scenario of copper-based fungicide application) and supporting results and discussion (model performance, regional prediction, limit of the approach).

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Author contributions

B.D., S.P. and G.I. designed research, B.D. performed research; S.P., J.A., R.M., G.T., P.P., L. M. and P.B. contributed to the acquisition of data/soil samples; B.D. and S.P.

analyzed data; and B.D., S.P. and G.I. wrote the manuscript with critical review from all authors. The authors declare no conflict of interest.

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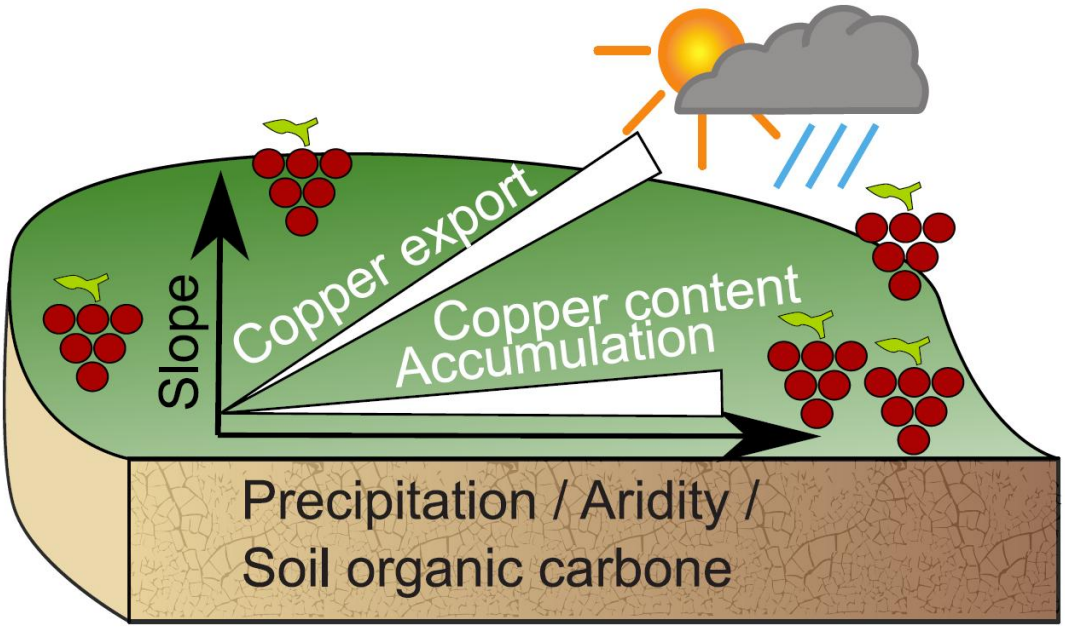
Slope
Copper export
Copper content
Accumulation
Precipitation / Aridity /
Soil organic carbone

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